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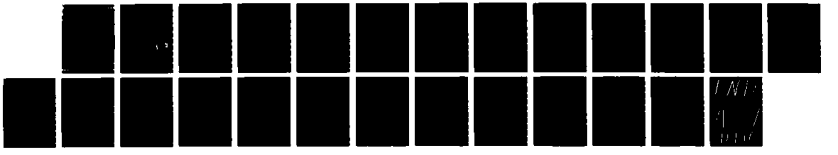

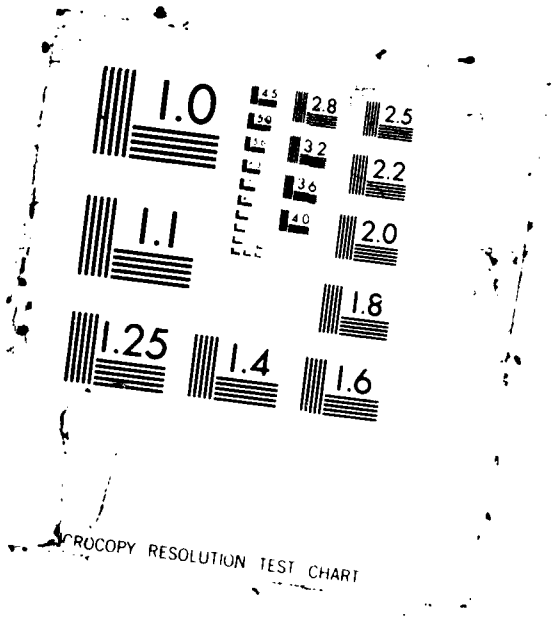
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Research progress on an alternative method to ab initio variational and perturbative approaches for the electronic structure of molecules is described. Progress in the report year on the evaluation of (1) molecular properties, (2) energy derivatives with respect to coordinates, and (3) excited states with the same symmetry as the ground state is described.

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Annual Summary Report

Quantum Monte Carlo for Molecules

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Description of Problem and Approach

Introduction.

In the last few years, Monte Carlo approaches have enjoyed ever wider application in the treatment of problems in theoretical physics [1]. The Monte Carlo method is statistical in nature, based on the generation of "random" numbers or "coin tosses." Thus it is perhaps easy to imagine using the Monte Carlo method for treating inherently statistical models. It is, however, also readily applied to problems of numerical integration [2]. How to solve many-body equations such as the Schrödinger equation by Monte Carlo is far less obvious. Nevertheless, many-body problems and the Schrödinger equation are readily treated by Monte Carlo.

Our focus here is on the quantum mechanical Monte Carlo (or QMC) methods [3]. These are the methods that explicitly treat the quantum aspects of a problem, such as solving the Schrödinger equation. This is done statistically by the simulation of an appropriate random process. In particular, the formal similarity of the Schrödinger equation with a diffusion equation allows one to calculate quantum mechanical expectation values as Monte Carlo averages over an

ensemble of appropriately chosen random walks. The method is procedurally quite simple. As a result, QMC provides an attractive alternative to the conventional variational and perturbation-theoretic techniques used in physics and chemistry.

Past Work

We have applied QMC sucessfully to the calculation of the total energy of a number of molecular systems [4-7]. In every case we have achieved very high accuracy compared with experimentally inferred and exact results (where available), as well as *ab initio* configuration interaction calculations. In most cases, 90-100% of the correlation energy has been obtained.

More recently this research program has also begun to make a significant contribution [5-7] to obtaining quantities of such physical interest as electron affinities, ionization potentials, binding energies, reaction barriers, level splittings, and so on. Since much of chemistry takes place predominantly in the valence electrons of a system, the quantities of interest are usually small differences of large total energies. Calculations for such difference quantities are a far more difficult task for Monte Carlo, since a small statistical uncertainty (e.g. of as little as 0.1%) in the separate total energies can mask the sought-after energy difference. To reduce the statistical error to the level needed by "brute force" is costly in computer time, as the standard deviation decreases only as $(CPU\ time)^{-\frac{1}{2}}$. Algorithmic developments, such as differential QMC [8] have undergone preliminary development and hold promise for reductions in variance through correlated sampling techniques. Another avenue utilizes the zero-

variance property of the approach: the variance vanishes as a trial wave function Ψ_T approaches the true eigenfunction. To attempt to take advantage of this, we have previously developed an iterative procedure for improving Ψ_T [7]. Recently, we have also devised improved forms of correlation factors for use with SCF trial wave functions, and methods of Monte Carlo optimization of the correlation parameters.

More specific examples of systems we have treated include selected points along the reaction coordinate of the H + H_2 exchange reaction [6], with particular emphasis on the saddle-point geometry for which Liu [9] has performed the most extensive CI calculation to date. The bound for the barrier height which we obtained by QMC is 0.16 kcal/mole *below* Liu's bound, and probably lies within 0.1 kcal/mole of the exact answer. In addition, we were able to obtain these results with only single-determinant trial functions, and a basis set expansion at only the double-zeta level.

Until recently, most QMC applications have been limited to calculation of energies of ground states and lowest states of a given symmetry. As an example of the latter, we calculated the singlet-triplet splitting in methylene [7]. The two states studied are both lowest-energy states of their respective symmetries. In these studies, the accuracies obtained with QMC have been comparable to the best achieved by conventional *ab initio* methods. In the next section, we discuss our recent work extending QMC to excited states of the same symmetry as the ground state. We also report on calculations of properties unrelated to the energy such as moments of the charge distribution, and transition dipole

moments.

In addition to properties, it is certainly useful to be able to compute the analytic gradient of the energy with respect to nuclear coordinates in order to determine forces, and thereby equilibrium and transition state geometries [10] and (by finite difference or higher analytic derivatives) harmonic vibrational frequencies [11]. In the recent past we have implemented QMC methods for doing these calculations. They are currently working, but need improvement, especially with respect to efficiency. Using this approach, we have performed calculations on H_2 at a few nuclear separations [12]. QMC is competitive with CI, and far superior to Hartree-Fock. The combination of QMC energy points with the additional information available from the derivatives has allowed us to reconstruct the potential-energy curve of H_2 from just four QMC data points. The Monte Carlo potential-energy curve so obtained is indistinguishable from the exact one [13].

QMC Theory

Briefly, one simulates a quantum molecular system by allowing it to evolve under the time-dependent Schrödinger equation in imaginary time. It is easy to show [4] that the use of imaginary time causes the system to approach a stationary state which is the lowest state of a given symmetry. Many properties may then be "measured" as averages over the resulting equilibrium distribution.

By writing the imaginary-time Schrödinger equation with a shift in the zero of energy as

$$\frac{\partial \Psi(\underline{R},t)}{\partial t} = D\,\nabla^2\Psi(\underline{R},t) + [E_T - V(\underline{R})]\Psi(\underline{R},t)\ . \qquad (1)$$

we see that this equation is a generalized diffusion equation. The first term on the right-hand-side is the ordinary diffusion term, while the second term is a position-dependent rate (or branching) term. For an electronic system, $D = \hbar^2/2m_e$, $\underline{R}$ is the three-N dimensional coordinate vector of the N electrons, and $V(\underline{R})$ is the Coulomb potential. Since diffusion is the continuum limit of a random walk, one may simulate Eq. (1) with the function Ψ (note, *not* Ψ^2) as the density of "walks". The walks undergo an exponential birth and death as given by the rate term. This connection between a quantum system and a random walk was first noted by Metropolis, who attributes it to Fermi [14].

The steady-state solution to Eq. (1) is the time-independent Schrödinger equation. Thus we have $\Psi(\underline{R},t) \rightarrow \phi(\underline{R})$, where ϕ is an energy eigenstate. The value of E_T at which the population of walkers is asymptotically constant gives the energy eigenvalue. Early calculations employing Eq. (1) in this way were done by Anderson on a number of one- to four-electron systems [15].

Unfortunately, in order to treat systems larger than two electrons, the Fermi nature of the electrons must be taken into account. The antisymmetry of the eigenfunction implies that Ψ must change sign; however, a density (e.g. of walkers) cannot be negative. To handle this, Anderson made simplifying assumptions about the positions of the nodes. His method was *ad hoc* , and not readily generalizable. Another method which imposes the antisymmetry, and at the same time provides more efficient sampling (thereby reducing the statistical "noise"), is importance sampling with an antisymmetric trial function Ψ_T (see e.g. Ref. 4). The zeroes (nodes) of Ψ_T become absorbing boundaries for the diffusion process;

this maintains the antisymmetry. The additional boundary condition that Ψ vanish at the nodes of Ψ_T is the fixed-node approximation [4,16]. The magnitude of the error thus introduced depends on the quality of the *nodes* of $\Psi_T(\underline{R})$, and vanishes as Ψ_T approaches the true eigenfunction. To the extent that Ψ_T is a good approximation of the wave function, the true eigenfunction is almost certainly quite small near the nodes of Ψ_T. Thus one expects the fixed-node error to be small for reasonable choices of Ψ_T. Work on a number of systems has borne this out [4-7,17,18]. In addition, this error is variationally bounded.

To implement importance sampling and the fixed-node approximation, Eq. (1) is multiplied by Ψ_T, and rewritten in terms of the new probability density $f(\underline{R},t)=\Psi_T(\underline{R})\Psi(\underline{R},t)$. The resultant equation for $f(\underline{R},t)$ may be written

$$\frac{\partial f}{\partial t} = D\nabla^2 f + [E_T - E_L(\underline{R})]f - D\nabla\cdot[f F(\underline{R})] \quad . \tag{2}$$

The local energy $E_L(\underline{R})$, and the local velocity field $F(\underline{R})$ are simple functions of Ψ_T given by

$$E_L(\underline{R}) \equiv H\Psi_T(\underline{R})/\Psi_T(\underline{R}) \quad , \tag{3a}$$

and

$$F(\underline{R}) \equiv 2\nabla\Psi_T(\underline{R})/\Psi_T(\underline{R}) \quad . \tag{3b}$$

Equation (2), like Eq. (1), is a generalized diffusion equation, though now with the addition of a drift term due to the presence of F.

In order to perform the random walk implied by Eq. (2) we use a short-time approximation to the Green's function. The Green's function is used to evolve the distribution forward in time, i.e. $f(\underline{R},t)\rightarrow f(\underline{R}',t+\tau)$. This process is iterated to large t. Such an approach becomes exact in the limit of vanishing

time-step size, τ. Asymptotically, $f(\underline{R},t)\rightarrow f_\infty(\underline{R})=\Psi_T(\underline{R})\hat{\phi}(\underline{R})$.

The function $\hat{\phi}(\underline{R})$ is the lowest-energy eigenfunction of the Schrödinger equation for the imposed set of nodes. Although neither this function nor f_∞ is known analytically, we can nevertheless sample desired quantities from the equilibrium distribution. Averages taken with respect to the distribution f_∞ are known as mixed averages. For example, sampling a quantity A in equilibrium after N samples gives the average (in the limit of large N)

$$\frac{1}{N}\sum_{configs} A = <A>_{f_\infty}$$

$$\equiv \int f_\infty(\underline{R})\, A \; d\underline{R} \tag{4}$$

$$= \frac{\int \Psi_T(\underline{R})\hat{\phi}(\underline{R})\, A \; d\underline{R}}{\int \Psi_T(\underline{R})\hat{\phi}(\underline{R})\, d\underline{R}} .$$

or in abbreviated Dirac notation (with the normalization absorbed),

$$<A>_{f_\infty}=<\Psi_T \mid A \mid \hat{\phi}> . \tag{5}$$

On the other hand, the correct expectation value of A, for a state $\hat{\phi}$, is $<\hat{\phi} \mid A \mid \hat{\phi}>$. In computing the energy, or any property for which $\hat{\phi}$ is an eigenstate, there is no difference between these two averages. This follows since the eigenvalue can be taken out of the integral in the numerator of Eq. 4. In particular, to compute the energy one samples the local energy $E_L(\underline{R})$. Then

$$<E>=\frac{\int \hat{\phi}(\underline{R})\Psi_T(\underline{R})[\Psi_T^{-1}(\underline{R})H\Psi_T(\underline{R})]\, d\underline{R}}{\int \hat{\phi}(\underline{R})\Psi_T(\underline{R})\, d\underline{R}}$$

$$=<\hat{\phi} \mid H \mid \Psi_\infty>=\hat{E}_0 , \tag{6}$$

where $\hat{E}_0$ is the eigenvalue corresponding to the state $\hat{\phi}$. The last equality

follows upon noting that H is Hermitian, and thus can operate to the left.

For expectation values of quantities whose operators do not commute with H, the mixed average of Eq. 5 is only approximate. One suspects that the mixed average is in some sense "half-way" between the exact expectation value (with respect to $\hat{\phi}$) and the variational expectation value, taken with respect to the trial wave function, i.e. $<\Psi_T \mid A \mid \Psi_T>$. Taken literally, this implies that

$$<\hat{\phi} \mid A \mid \hat{\phi}>=2<\Psi_T \mid A \mid \hat{\phi}>-<\Psi_T \mid A \mid \Psi_T> . \tag{7}$$

This result can be readily formalized [19] and gives an approximate formula for expectation values taken solely with respect to $\hat{\phi}$ from just mixed and variational averages. However, it is difficult to judge how accurate this approximation is. Thus, it is desirable to be able to sample exactly from the distribution $\mid \hat{\phi} \mid^2$. This can be done, though with some changes to the usual QMC algorithm. The distribution f_∞ must be weighted locally by $\hat{\phi}(\underline{R})/\Psi_T(\underline{R})$. This quantity is essentially the asymptotic number of survivors of the local configuration $\underline{R}$ [20]. Thus, algorithmically, one must follow each configuration into the future before computing any averages. Our results have shown that while the variational approximation is poor, the approximate formula (7) is quite good, and excellent agreement with exact results is obtained by sampling from the pure $\mid \hat{\phi} \mid^2$ distribution.

Progress in Current Year

(1) *Excited States.* As mentioned in Sect. I, work with QMC has been essentially limited to ground-state potential-energy surfaces and lowest-energy states of a particular symmetry [4-7,18]. Examples include our calculation of the energy of the first excited state of methylene [7] in order to obtain the (until recently) elusive singlet-triplet splitting. Our results there are in excellent agreement with the most recent experiments. The restriction on lowest energy states of a symmetry comes from an essential feature of the mapping of the Schrödinger equation into its diffusion analog—namely, that time in these two equations differs by a factor of i. This means that the expansion of a time-dependent molecular state vector in energy eigenfunctions multiplied by $\exp(-iEt/\hbar)$, results in a series in which only the lowest energy term (i.e. $\hat{\phi}$) survives at large t. Thus one obtains exponential convergence to the lowest energy eigenstate.

If Ψ_T is orthogonal to the exact lowest-energy state, one can see from Eq. 6 that convergence will be to the next-lowest energy. (Initially $\hat{\phi}$ contains a superposition of states.) This fact actually is used even in the calculation of molecular ground-state energies, as Fermi states are excited states (with respect to the Boson ground state) of the Schrödinger equation. By choosing Ψ_T to be antisymmetric with respect to particle exchange, one can project out all symmetric states. A similar result holds for calculations of different symmetry states of a given molecule.

When studying states of the same symmetry, it is generally not possible to find a trial wave function exactly orthogonal to all the lower-energy states of that

symmetry. This implies that convergence will ultimately be to the lowest-energy state. However, the fixed-node approximation used to treat the Fermi problem may be used to advantage here. In the fixed-node approximation, the nodes of Ψ_T are used to divide $\underline{R}$-space into separate volume elements. The Schrödinger equation is solved separately in each of these elements. This results in a solution of the Schrödinger equation with added boundary conditions. Viewed this way, the Fermi problem is handled by forcing the generation of an antisymmetric state above the Bose ground state through the placement of nodes in the solution $\hat{\phi}$. In like manner, other excited states can be treated approximately by imposing additional nodes. The accuracy of the approximation will depend on how well these nodes are placed.

In treating excited states, traditional *ab initio* methods generate wave functions with the correct number and dimensionality of nodes. Thus such wave functions are a good place to begin in searching for an excited-state Ψ_T. This year we have used QMC in this way, and explored the type of trial wave functions required for accurate nodal representation [21].

We have explored the effects of basis set and number of reference configurations on the convergence of the QMC energies. At least for a small number of determinants, results do improve with the number of reference configurations (see Table 1). Quite possibly, after a certain level of calculation no noticable improvements will result. For the ground states studied to date this has indeed been the case, where a single determinant and a double-zeta expansion level have been that level.

We are also exploring a new approach for calculating excited states. In this method, all (i.e. a significant number, say 10) excited states are found in a single calculation. At the present time, in order to avoid problems with Fermi statistics, we are restricting ourselves to vibrational and rotational states through the use of potential energy surfaces. This restriction can be lifted, and excited electronic states will be explored at a later time.

The method involves the calculation of correlation functions. In particular, we calculate the following matrices of correlation functions

$$N_{\alpha\beta}(t)=<\Psi_\alpha(t)\mid\Psi_\beta(0)> \tag{8}$$

and

$$E_{\alpha\beta}(t)=<\Psi_\alpha(t)\mid H\mid\Psi_\beta(0)> \tag{9}$$

Here $\{\Psi_\alpha(0)\}$ is a set of M trial wave functions, representing guesses at the first M states of the system, and $\Psi_\alpha(t)=e^{-tH}\Psi_\alpha(0)$. The eigenvalues of E/N then give the first M eigenvalues of H. Briefly, we seek the values of λ that are solutions to

$$\det(E-\lambda N)=0\ . \tag{10}$$

Expanding Ψ_α in a complete set of states $\{\phi_i\}$ we have

$$\Psi_\alpha=\sum_i c_i^{\alpha}\, e^{-E_i t}\,\phi_i\ . \tag{11}$$

Using the Binet-Cauchy theorem for rectangular matrix products, we obtain

$$\det(E-\lambda N)=\sum_{i_1<i_2<\cdots<i_M} z_{i_1}z_{i_2}\cdots z_{i_M}\mid D_{i_1\cdots i_M}\mid^2 \tag{12}$$

where $z_i=(E_i-\lambda)e^{-E_i t}$ and $\mid D_{i_1\cdots i_M}\mid=\det\mid c_{i_\mu}^{\nu}\mid$. Thus, asymptotically (i.e. $t\to\infty$), the dominant term in (12) is

$$(E_0-\lambda)(E_1-\lambda)...(E_M-\lambda)e^{-E_0 t}\, e^{-E_1 t} \cdots e^{-E_M t} \mid D_{1\ M} \mid , \tag{13}$$

and consequently, the eigenvalues are indeed the first M eigenvalues of the Hamiltonian. One constraint is that each of the actual M lowest eigenfunctions of H must have a non-zero overlap with at least one of the Ψ_α. If this is not so, the M states obtained will exclude those states with zero overlap.

In order to compute the correlation matrices of Eqs (8) and (9), let us write

$$\begin{aligned} E_{\alpha\beta}(t) &= <\Psi_\alpha(\underline{R}') \mid He^{-tH} \mid \Psi_\beta(\underline{R})> \\ &= \int \frac{H\Psi_\alpha(\underline{R}')}{\Psi_g(\underline{R}')} \left[\Psi_g(\underline{R}') e^{-tH} \frac{1}{\Psi_g(\underline{R})} \right] \frac{\Psi_\beta(\underline{R})}{\Psi_g(\underline{R})} \left| \Psi_g(\underline{R}) \right|^2 d\underline{R}\ d\underline{R}' \\ &= <E_L^\alpha(\underline{R}') e^{-\int_0^t dt' E_L(t')} w^\beta(\underline{R})>_{|\Psi_g|^2} \\ &= <<E_L^\alpha(\underline{R}'(t+\tau)) e^{-\int_\tau^{t+\tau} dt' E_L(t')} w^\beta(\underline{R}(\tau))>_{|\Psi_g|^2}> , \end{aligned} \tag{14a}$$

where the bracketed quantity [. . .] is the usual QMC Green's function which propagates the guiding function (Ψ_g) times the wave function at $\underline{R}$ to $\Psi_g(\underline{R}')\Psi(\underline{R}')$; $E_L^\alpha \equiv H\Psi_\alpha/\Psi_g$; E_L^g is the usual local energy associated with a function Ψ_g ; $w^\beta \equiv \Psi_\beta/\Psi_g$; and the outer average $< \ldots >$ in the final line is an average over τ, corresponding to an average over choices of origin for the random walk. For this last equality to be valid, one must have ergodicity for the random walk being described by the Green's function. Replacing E_L^α in the final line by w^α gives the correlation matrix $N_{\alpha\beta}(t)$. Finally, note that if $\Psi_\alpha = \Psi_\beta = \Psi_g = \Psi_T$ this approach reduces to the usual QMC.

An alternative expression that is perhaps more transparent because of the similarity of its development to the usual QMC arguments begins with Eq. (9):

$$E_{\alpha\beta}(t) = \langle \Psi_\alpha(t) \mid H \mid \Psi_\beta(0) \rangle = \int \frac{H\Psi_\beta(\underline{R},0)}{\Psi_g(\underline{R},0)} \Psi_g(\underline{R},0) \frac{\Psi_\alpha(\underline{R},t)}{\Psi_g(\underline{R},t)} \Psi_g(\underline{R},t)\, d\underline{R}$$

$$= \left\langle \frac{H\Psi_\beta(0)}{\Psi_g(0)} \frac{\Psi_\alpha(t)}{\Psi_g(t)} \right\rangle_{\Psi_g(0)\Psi_g(t)} \quad (14b)$$

Though different in form, this expression is equivalent to Eq. (14a).

As a test of this method, we have studied the H_2O molecule, for which there are a number of good potential-energy surfaces, as well as other theoretical and experimental results on vibrational excited states. Our numerical results are only preliminary. Using only 2 minutes of VAX 8600 cpu time, we found the ground-state energy exact to 0.2%, and the first five excited states to within 10%. Since these are already the vibrational frequencies, 10% is not too bad. Nevertheless, we expect these results can be significantly improved. The reason for the much larger noise in the excited states is due to the fact that all the trial functions $\Psi_\alpha(t)$ approach the ground state at large time. Thus, noise in the matrix elements of Eqs. 8 and 9 grows exponentially.

(2) *Molecular Properties.* Our work on properties unrelated to the energy—for which averages from the true distribution $|\hat{\phi}|^2$ must be used—has been quite successful. The theory is described in Sect. I.3 above and will not be repeated here. Much of our current work has involved gaining additional experience analogous to what we have already gained in studies of ground-state energies. We have discovered some Ψ_T dependence for certain properties (e.g. dipole moments). Basis-set expansions and multi-determinant Ψ_T's need to be explored. Further, an understanding must be gained of why the averages with respect to $|\hat{\phi}|^2$ should be trial-function sensitive. It is clear how polarization

functions can dramatically affect dipole moments computed with respect to $|\Psi_T|^2$; such effects should, however, be irrelevant with the correct $|\hat{\phi}|^2$ averaging procedure. The only approximation is the nodal positioning. Thus we also wish to understand how placement of these nodes affects properties. Some results for dipole and quadrupole moments of various molecules are presented in Table 2.

(3) *Matrix Elements Between Different Electronic States.* Thus far we have been discussing the calculation of expectation values of the form $<\Psi_T | A | \Psi_T>$ or $<\hat{\phi} | A | \Psi_T>$ or $<\hat{\phi} | A | \hat{\phi}>$. Here Ψ_T and $\hat{\phi}$ are approximate forms for the same state. Matrix elements for operators causing transitions between different states, such as $<\hat{\phi}_1 | x | \hat{\phi}_2>$, are of particular importance for the study of absorption of radiation in molecules. We are developing QMC methods for these problems. Theoretical development is currently proceeding, and is summarized here. This effort also ties in with our other work including calculations of expectation values of operators such as x, and of excited-state properties.

As mentioned above, the object is to compute matrix elements of the type

$$T = <\hat{\phi}_1 | f(\underline{R}) | \hat{\phi}_2> \tag{15}$$

Here $f(\underline{R})$ is an arbitrary function of the electronic coordinates. The states $\hat{\phi}_1$ and $\hat{\phi}_2$ are different eigenfunctions of the Hamiltonian in the Born-Oppenheimer approximation. As described in the theory section, standard QMC application provides expectation values for a quantity $Q(R)$ of the form

$$<Q>=\int Q(\underline{R})\Psi_{T_1}(\underline{R})\hat{\phi}_1(\underline{R})d\underline{R}\,/\int\Psi_{T_1}(\underline{R})\hat{\phi}_1(\underline{R})d\underline{R} \tag{16}$$

where $\Psi_{T_1}(\underline{R})$ is a trial or guiding function corresponding to the eigenstate $\hat{\phi}_1$. The idea is to choose $Q(\underline{R})$ in such a way as to obtain T.

First let us write $Q(\underline{R})\equiv h(\underline{R})w(\underline{R})$. By properly choosing the weight $w(\underline{R})$ one can introduce the state $\hat{\phi}_2$. Namely, if one uses a trial function Ψ_{T_2} as a guiding function to propagate random walks forward from $\underline{R}$, the asymptotic number of walkers converges to

$$w(\underline{R})=\exp[-(E_2-E_{T_2})t]<\Psi_{T_2}\mid\hat{\phi}_2>\hat{\phi}_2(\underline{R})/\Psi_{T_2}(\underline{R}). \tag{17}$$

Here E_{T_2} is a trial energy chosen as close as possible to the energy E_2 of the the state $\hat{\phi}_2$, and t is the time duration that the walk has been propagating from point $\underline{R}$. In practice, convergence of $w(\underline{R})$ is very rapid. Choosing $E_{T_2}=E_2$ thus leads to

$$<Q>=\frac{<\Psi_{T_2}\mid\hat{\phi}_2>}{<\Psi_{T_1}\mid\hat{\phi}_1>}\int h(\underline{R})\frac{\Psi_{T_1}(\underline{R})}{\Psi_{T_2}(\underline{R})}\hat{\phi}_1(\underline{R})\hat{\phi}_2(\underline{R})d\underline{R}\,. \tag{18}$$

It is thus apparent that choosing $h(\underline{R})=f(\underline{R})\Psi_{T_2}(\underline{R})/\Psi_{T_1}(\underline{R})$ yields

$$<Q>=\frac{<\Psi_{T_2}\mid\hat{\phi}_2>}{<\Psi_{T_1}\mid\hat{\phi}_1>}T\,. \tag{19}$$

Given fairly accurate, normalized trial functions, the two overlap integrals in Eq. (19) should both be close to (but less than) unity. Thus one can compute the desired matrix element. If necessary, QMC may be employed to compute the overlap integrals, to eliminate this approximation.

Thus far this method has only been tested on the hydrogen atom. The results show that the method works, though more realistic problems need to be addressed. Table 3 shows the results of our preliminary work.

List of Manuscripts for Current Summary Year

1. "Quantum Chemistry by Quantum Monte Carlo: Beyond Ground-State Energy Calculations" P. J. Reynolds, R. N. Barnett, B. L. Hammond, R. M. Grimes, and W. A. Lester, Jr., Int. J. Quant. Chem. 29, 589 (1986).

2. "Molecular Physics and Chemistry Applications of Quantum Monte Carlo" P. J. Reynolds, R. N. Barnett, B. L. Hammond, and W. A. Lester, Jr., J. Stat. Phys. 43, 1017 (1986).

3. "Quantum Monte Carlo Approach to Electronically Excited Molecules," R. M. Grimes, B. L. Hammond, P. J. Reynolds, and W. A. Lester, Jr., J. Chem. Phys. 85, 4749 (1986).

4. "Exact Monte Carlo for Molecules," W. A. Lester, Jr. and P. J. Reynolds, in Proceedings of the Florida A & M Spring Science Seminars, *in press*.

5. "Quantum Monte Carlo for Molecules," P. J. Reynolds and W. A. Lester, Jr. in *Physics in the News 1985*, Physics Today 39, S-14 (1986).

6. "Is Quantum Monte Carlo Competitive? Lithium Hydride Test Case," R. N. Barnett, P. J. Reynolds, and W. A. Lester, Jr., J. Phys. Chem. *in press*.

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Table 1. Comparison of the energy of excited singlet states of H_2 ($B\ ^1\Sigma_u^+$) and ($E\ ^1\Sigma_g^+$) at their equilibrium geometries with self-consistent field (SCF), configuration interaction (CI) and exact results. For QMC, several trial functions are used. They are constructed from double-zeta (DZ) and double-zeta-plus-polarization (DZP) SCF functions. The column headed % CE gives the percentage of correlation energy recovered. Statistical uncertainties are indicated in parentheses.

Method	H_2 ($B\ ^1\Sigma_u^+$)			H_2 ($E\ ^1\Sigma_g^+$)		
	E (h)	% CE	$\Delta(E - E_{exact})$ (kcal/mole)	E (h)	% CE	$\Delta(E - E_{exact})$ (kcal/mole)
MCSCF[a]	-0.7415	0	9.4	-0.7036	0	9.1
CI[b]	-0.7553	90	0.9	-0.7152	79	1.8
QMC (DZ)	-0.748(2)	41	5.6	—	—	—
QMC (DZP)	-0.7536(3)	79	1.9	—	—	—
QMC 8 det. (DZP)	-0.7563(9)	97	0.3	-0.7174(8)	95	0.4
Exact[c]	-0.7567	100	0.0	-0.7181	100	0.0

[a] Ref. 21.
[b] Ref. 22.
[c] Ref. 23.

Table 2. Dipole and quadrupole moments for various molecules. Units are Debyes for the dipole moments and esu-cm$^2\times10^{-26}$ for the quadrupole moments. "Approximate Formula" refers to Eq. 7 of the text. Statistical uncertainties are indicated in parentheses.

Method	H_2	N_2	LiH		BH	
	Q	Q	μ	Q	μ	Q
$\langle\Psi_T\vert A \vert\Psi_T\rangle$	0.49(1)	-2.19(4)	5.898(20)	-4.32(3)	1.75(4)	-4.39(2)
$\langle\Psi_T\vert A \vert\hat{\phi}\rangle$	0.56(2)	-1.80(10)	5.921(12)	-4.24(3)	1.62(4)	-4.12(5)
Approximate Formula	0.63(5)	-1.41(20)	5.944(31)	-4.16(7)	1.49(8)	-3.85(6)
$\langle\hat{\phi}\vert A \vert\hat{\phi}\rangle$	0.61(3)	---	5.885(20)	-4.04(5)	1.44(7)	-4.02(12)
Hartree-Fock	0.664[a]	-1.29[c]	6.003[e]	-4.51[e]	1.74[h]	-3.60[h]
MCSCF	---	-1.22[c]	5.826[f]	-4.13[f]	1.32[i]	-3.10[i]
Experiment or Exact	0.61[b]	-1.4(1)[d]	5.828[g]	---	1.27(21)[j]	---

[a] Ref. 24.
[b] Ref. 25.
[c] Ref. 26.
[d] Ref. 27.
[e] Ref. 28.
[f] Ref. 29.
[g] Ref. 30.
[h] Ref. 31.
[i] Ref. 32.
[j] Ref. 33.

Table 3. Matrix elements between the 1s and 2s states of H.

$f(\underline{R})$	$<\phi_{1s} \mid f \mid \phi_{2s}>_{QMC}$	$<\phi_{1s} \mid f \mid \phi_{2s}>_{exact}$
r	-0.557(11)	-0.559
r^2	-2.92(7)	-2.98

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